REMARKS/ARGUMENTS

Reconsideration is respectfully requested.

Claims 1, 4, 6-7, and 9 are pending in the present application before this amendment. By the present amendment, Claim 4 has been canceled without prejudice, and Claim 1 has been amended. No new matter has been added.

Claims 1, 4, 6, and 9 stand rejected under 35 U.S.C. § 103(a) as being obvious over JP01-169749 (Takakubo et al.).

Claims 1, 4, 6, 7, and 9 are rejected under 35 U.S.C. § 103(a) as being obvious over Takakubo et al. in view of U.S. Patent No. 5,013,635 (Okhawa et al.).

In response, Claim 1 has been amended to incorporate the limitations of Claim 4, i.e., the hydrogenated amorphous carbon contains 5 to 60 atomic percent hydrogen, therein.

The properties of amorphous carbon films formed by PACVD techniques vary considerably with the conditions of the plasma deposition (see the enclosed Table 1, J. Robertson, "Amorphous Carbon", Advances In Physics, 1986, Vol. 35, No. 4, 317-374, and Table 1, B. Dischler, et al., "Infrared and Raman Analysis of Hydrogenated Amorphous Carbon Films...", ISPC-7 Eindhöven, 1985, paper number A-1-4, pages 45-52). The plasma deposition conditions (for example, 50-200 milli-Torrs, 250-550 volts) are relatively different from those (30 milli-Torrs, RF 100W) of Takakubo JP 01-169749, which results in a difference in the properties of the amorphous carbon film. Note that the properties of the amorphous carbon film of the presently claimed invention

permit absorption of the energy of the laser beam having a wavelength ranging from 300 to 900nm, which results in evolution of hydrogen gas in the amorphous carbon film, and that not all of the amorphous carbon films can absorb the energy of the laser beam in that wavelength range. In addition, the amorphous carbon film of this invention contains 5 to 60 atomic percent hydrogen, which is not disclosed in the cited Takakubo et al. reference.

Also enclosed are two more references, Tsai et al., Critical Review, "Characterization of diamond-like carbon films...", J. Vac. Sci. Technol. A 5 (6), Nov/Dec 1987, and H. Shimizu et al., "Microstructures of Hydrogenated Amorphous Carbon Films...", J. of Non-Crystalline Solids 114 (1989) 196-198, which Applicants submit to the USPTO for showing the difference between presently claimed invention and the cited Takakubo et al. reference.

Further to our above Remarks/Arguments with respect to the difference in the plasma deposition conditions between the presently claimed invention and the Takakubo et al. reference, Applicants note that the amorphous carbon film of Takakubo et al. reference is an i-carbon film, i.e., a diamond-like carbon film (Tsai et al. on page 3288, left column, last line 4), which contains very few hydrogen atoms (Takakubo et al, the abstract; Tsai et al., page 3290, left column, lines 1-7, and page 3291, the last deposition system listed in Table II). Note that diamond is free of hydrogen, which explains why the diamond-like amorphous carbon film contains very few hydrogen atoms. Unlike the cited Takakubo et al. reference, the hydrogenated amorphous carbon film of the presently claimed invention contains a relatively large amount of hydrogen

atoms, which consist of C-H bonds, is not an i-carbon or a diamond-like amorphous carbon film, and permits evolution of hydrogen gas therein when heated to about 350°C by a laser beam with a wavelength ranging from 300 to 900 nm.

The Takakubo et al. reference employs a relatively large amount of hydrogen gas in the deposition system, which is a technique well known in the art for forming diamond-like amorphous carbon films. In CH_4+H_2 plasma deposition system (see Tsai, page 3291, the last deposition system listed in Table II; and Shimizu et al., page 198, left column, lines 6-9), hydrogen radicals selectively and actively attack C-H bonds to extract and to strip off the hydrogen atoms from the C-H bonds during deposition so as to permit accumulation of C-C bonds on the substrate, which results in formation of a diamond-like amorphous carbon film on the substrate.

The deposition system and conditions of the presently claimed invention are different from those of the Takakubo et al. reference, and the hydrogen atomic concentration as recited in the proposed amended claim 1 is not disclosed in the Takakubo et al. reference.

Accordingly, it is respectfully submitted that Claim 1, as amended, is not taught or suggested by either Takakubo et al. or Ohkawa et al., whether they are considered individually or taken together.

For the reasons set forth above, Applicants respectfully submit that Claims 1, 6-7, and 9, now pending in this application, are in condition for allowance over the cited references. This amendment is considered to be

responsive to all points raised in the Office Action. Accordingly, Applicants respectfully request reconsideration and withdrawal of the outstanding rejections and earnestly solicit an indication of allowable subject matter. Should the Examiner have any remaining questions or concerns, the Examiner is encouraged to contact the undersigned attorney by telephone to expeditiously resolve such concerns.

Respectfully submitted,

Dated: July 6, 2004

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Amorphous carbon

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Abstract

The properties of various types of amorphous carbon and hydrogenated amorphous carbon are reviewed with particular emphasis on the effect of atomic structure on the electronic structure. It is shown how the proportion of sp^3 and sp^2 sites not only defines the short-range order but also a substantial medium-range order. Medium-range order is particularly important in amorphous carbon because it is the source of its optical gap, whereas short-range order is usually sufficient to guarantee a gap in other amorphous semiconductors. The review discusses the following properties: short-range order and the radial distribution function, mechanical strength, the electronic structure, infrared and Raman spectra, optical properties, electron energy-loss spectra, core-level photoemission spectra, electrical conductivity, electronic defects and the electronic excitation spectra, doping of hydrogenated amorphous carbon.

Contents

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Table 1 gives values of some of the key properties for diamond, graphite and four forms of disordered carbon. Diamond consists of sp^3 sites. The saturated bonding produces the wide 5·5 eV band gap and low conductivity, and the isotropy of the bonding gives it its strength. Graphite consists of hexagonal layers of sp^2 sites, weakly bonded together by van der Waals forces into a ABAB stacking sequence along the c axis. Conductivity and strength are high along the basal plane but are low along the c axis. As graphite is the stable allotrope of carbon, many disordered forms of carbon have structures based on its lattice. The structures of μc-carbon and glassy carbon are frequently classified in terms of a basal plane correlation length L_a and a c axis correlation length L_c, and table 1 shows that both materials are essentially metallic. Evaporated a-C and a-C:H differ from glassy carbon in being truly amorphous and semiconducting. The presence of a semiconducting band gap is a crucial difference and their structures are not so easily classified. It is now wise to derive the structure of both materials from first principles; first defining the proportion of sp^2 and sp^3 sites, then their local arrangement and finally, in a-C:H, the proportion and arrangement of the hydrogen atoms. Summarizing the data discussed in detail in later sections, it is generally believed that glassy carbon contains approximately 100% sp^2 sites, evaporated a-C 1–10% sp^3 sites, while a-C:H may comprise 30–60% hydrogen with perhaps 30% of the carbon sites having an sp^2 configuration, but this is strongly dependent on heat-treatment. Ion-beam deposition methods are able to raise the proportion of sp^3 sites in both a-C and a-C:H and produce harder films. There is little evidence for sp^1 sites in unhydrogenated carbons, but there is some evidence for minor amounts of $-C{\equiv}CH$ groups being present in a-C:H.

These two parameters, the carbon bonding and the hydrogen content, define the short-range order in amorphous carbon. However, they do not entirely define its structure. This is because there exists a substantial degree of medium-range order on the ~10 Å scale; the sp^2 sites of a-C tend to occur in warped graphite layer clusters and the sp^2 and sp^3 sites in a-C:H are somewhat segregated and clustered.

The structure of amorphous carbon is of fundamental importance for a variety of reasons, of particular interest here is the effect of disorder in a π electron system. Since the π states are weakly bound, they lie closer to the Fermi level E_F than the σ states (figure 2). Consequently, the filled π states will form the valence band and the empty π^* states will form the conduction band and so determine the size of the gap.

Table 1. Room-temperature conductivity (σ_{RT}), optical gap, density and hardness of forms of diamond, graphite glassy carbon, evaporated a-C, ion-beam deposited a-C, and plasma/ion-beam deposited a-C:H. References: 1 Dischler and Brandt (1985), 2 Moore (1973), 3 Jenkins and Kawamura (1976), 4 Noda *et al.* (1969), 5 Hauser (1975), 6 Fink *et al.* (1983), 7 Savvides (1986), 8 Zelez (1983) 9 Kaplan *et al.* (1985), and 10 Weissmantel *et al.* (1982).

	σ_{RT} (Ω^{-1} cm^{-1})	E_g (eV)	Density (g cm^{-3})	Hardness (kg mm^{-2})	Reference
Diamond	10^{-18}	5·5	3·515	10^4	1
Graphite	$2{\cdot}5\times10^4$ ($\perp c$)	−0·04	2·267		2
Glassy carbon	10^2–10^3	10^{-2}	1·3–1·55	800–1200	3, 4
Evaporated a-C	~10^{-3}	0·4–0·7	~2·0	20–50	1, 5, 6
Ion-beam a-C	~10^{-2}	0·4–3·0	1·8–2·7		7, 8
a-C:H	10^{-7}–10^{-16}	1·5–4	1·4–1·8	1250–6000	1, 6, 9, 10

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INFRARED AND RAMAN ANALYSIS OF HYDROGENATED AMORPHOUS CARBON FILMS, PREPARED BY R.F. PLASMA DEPOSITION FROM C_6H_6 OR C_6D_6 VAPOUR

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ABSTRACT

IR vibrational absorption and UV/VIS transmission were analyzed for differently prepared amorphous carbon films (hard or polymerlike, hydrogenated or deuterated). Raman spectra of as-grown and thermally annealed a-C:H provide structural information.

1. INTRODUCTION

Hydrogenated amorphous carbon films (a-C:H) have received considerable interest /1-3/ due to their favourable properties including extreme hardness, infrared transparency and chemical inertness. Applications, e. g. as antireflective and protective optical coatings /3,4/ have stimulated studies on relations between the deposition conditions and the resulting film properties. It appears that the impact energy of the particles arriving at the surface during plasma or ion beam deposition has a major influence on the structure and the properties of the growing film /3,5/. Recently, the incorporation of hydrogen and the type of carbon bonding has been investigated using infrared /6,7,9/ and electron energy loss /8/ spectroscopy. In the present investigation, we analyzed the infrared spectra of four types of films, i. e. hard and polymerlike, hydrogenated and deuterated amorphous carbon films. We have tabulated the frequencies of 28 C-H, 28 C-D and 10 C-C vibrations, and we have analyzed the bonding for the different types of films. In addition Raman spectra of as-grown and annealed a-C:H films are reported.

2. EXPERIMENTAL

Hydrogenated or deuterated amorphous carbon films were prepared by r.f. plasma deposition from benzene (C_6H_6) or deuterated benzene (C_6D_6) onto negatively self-biased substrates (Ge, glass) as described previously /3/. Both types of films (hard and polymerlike) were prepared in the same plasma chamber, and the corresponding high and low impact energies were obtained by the combinations high voltage /lower pressure and low voltage /higher pressure (cf. Table 1). Transmission and reflection spectra were taken in the UV, VIS, NIR and IR on two ratio recording double beam spectrometers, i. e. Perkin Elmer Lambda 9 and 580 B. The spectra were processed on a Perkin Elmer 3600 data station to obtain normalized absorption, optical gap and refractive index, as described previously /3,10/. The Raman spectra were observed at 300 K with 0.8 µm thick a-C:H films on silicon substrates, excited by 50 mW of power at 514 µm.

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Table 1: Comparison of hard and polymerlike carbon films with respect to plasma deposition parameters and physical properties.

parameter or property	a-C:H, a-C:D (hard) range	a-C:H, a-C:D (hard) present samples	a-C_xH_y, a-C_xD_y (polymerlike) range	a-C_xH_y, a-C_xD_y (polymerlike) present samples
bias voltage (V)	400 - 1800	1000	80 - 100	100
C_6H_6 or C_6D_6 pressure (Pa)	1.3 - 5.5	3.2	5.5 - 6.5	6.1
impact energy (eV)	50 - 200		10 - 50	
deposition rate (µm/h)	0.5 - 20	6.6		0.2
density (g/cm^{-3})	1.5 - 1.8	1.65		1.3
refractive index n	1.8 - 2.2	2.0	1.6 - 1.8	1.65
optical gap (eV)	0.8 - 1.8	1.3	1.8 - 3.0	3.3
IR line width (cm^{-1})		75		25
CH_3: CH_2: CH (%)	0 : 40 : 60		25 : 60 : 15	
sp^3 : sp^2 : sp^1 (%)	68 : 30 : 2		53 : 45 : 2	

Critical Review
Characterization of diamondlike carbon films and their application as overcoats on thin-film media for magnetic recording

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This paper reviews and analyzes the literature on thin carbon layers with emphasis on their use as protective overcoats for thin-film magnetic media. We discuss carbon as a material, its preparation as a thin film, and review and evaluate various techniques for characterizing its thin-film properties.

CONTENTS

I. INTRODUCTION

Although thin-film media have not been as widely used in computer hard disks for data storage as particulate media, the potential advantages of thin films in achieving high-density recording make it worthwhile to overcome their practical problems. Eventually they are expected to replace the particulate systems as the primary media for magnetic recording.[1,2] However, in contrast with the particulate system, film media always require overcoats for wear and corrosion protection as well as underlayers for nucleation, adhesion, and magnetic properties control.[3] The overcoats are essential for reliable memory storage, because head–disk contact occurs intermittently and when the drive starts and stops. Without a wear-resistant overcoat, wear between the head and media can lead to readback signal amplitude loss with use or even catastrophic damage to the magnetic disk. Moreover, smaller head-to-medium spacing is necessary for achieving the higher storage densities, but the lowering of the head flying height increases the risk of head–disk interaction. Therefore it is often stated that tribology has become the most important factor in the future development of magnetic recording disk drives.[4] In order to operate the flying head at lower submicron spacings, it is necessary to develop new technology to solve the wear problem.

Unlike the particulate media in which the wear problem has been solved by the incorporation of hard particles into the magnetic coating, a continuous protective overcoat is required for thin-film media. This overcoat should be as thin as possible, resist wear by the head, have low static and dynamic friction coefficients with the head, and protect the medium against corrosion. One of the most promising candidates for such overcoats currently being explored is a hard carbon film.[3,5,6]

The multilayer structure of metal-film disks has introduced new tribological problems in the head–medium interface.[6] In order to solve these problems (associated with the development of state-of-the-art disks for computer memory) a basic understanding of the structure of overcoating carbon films is crucially important.

II. CARBON MATERIAL

Carbon occurs widely in its elemental form as crystalline and amorphous solids. Diamond and graphite are the two crystalline allotropes of carbon. The diamond crystal structure is face-centered cubic with interatomic distances of 0.154 nm.[7] Each atom is covalently bonded to four other carbon atoms (sp^3 tetragonal bonds). The structure of graphite is described as layers of carbon atoms with strong trigonal bonds (sp^2) with an interatomic distance of 0.1415 nm in the basal plane. The fourth electron in the outer shell forms a weak bond of the van der Waals type between planes and accounts for such properties of graphite as good electrical conductivity, lubricity, lower density, a grayish-black appearance, and softness, which are in contrast to the properties of diamond.

Carbon also exists in numerous amorphous forms, which

can be characterized as degenerate or imperfect graphitic structures, i.e., the layer planes are not oriented with respect to their common axis, the angular displacement of layers is random, and the layers overlap one another irregularly.[7] For instance, x-ray diffraction patterns of carbon black show two or three diffuse rings similar to the more intense rings of natural graphite, indicating that only short-range order exists in the amorphous carbon. Neutron and x-ray diffraction data show the predominately trigonal coordination in amorphous carbon.[8]

III. PREPARATION AND PROPERTIES OF CARBON THIN FILMS

Interest in depositing thin films of diamond has been motivated by the unique properties of this material and the demand of modern technologies, especially those associated with developments in the electronic industry. These properties include extreme hardness, chemical inertness, high electrical resistivity, high dielectric strength, optical transparency, and high thermal conductivity. Disregarding the earlier attempts to deposit diamond films epitaxially on diamond, the first diamondlike films were deposited by a beam of carbon ions produced in an argon plasma as reported by Aisenberg and Chabot,[9] and later confirmed by Spencer *et al.*[10] These carbon films are distinguished by a change from soft carbon deposits to exceptionally hard films as their resistivity rises from 0.1 to 10^{12} Ω cm and their optical properties change from those of graphite to those of a dielectric.[11] However, later research revealed that the prevailing atomic arrangement in these films is amorphous or quasiamorphous with small crystallites whose structures are yet to be identified unequivocally. It is noteworthy that in recent works, diamond particles[12] and diamond films,[13,14] including amorphous carbon, are reported to have been formed by chemical vapor deposition (CVD).

Following the first works, several alternative techniques have been developed for producing this unusual carbon film. The various methods include (1) a primary ion beam deposition of carbon ions with energies in excess of 40 eV, (2) sputter deposition of carbon films with or without bombardment by an intense flux of ions with energies of the order of 1 keV, (3) by deposition from an rf plasma, sustained in hydrocarbon gases, onto substrates negatively biased by about 100 eV, and (4) by ion beam plating of benzene or other hydrocarbons at acceleration voltages of 100 to 1000 V.[15,16] Whereas plasma-assisted CVD, i.e., method (3) and ion plating, method (4), have been mostly used to deposit hard carbon in nonrecording applications, in recording applications sputtering, method (2) is most desirable for high-volume processing.

The basic process that results in carbon films with the required unique properties involves electric charges (ions, electrons) in the crystallization process, i.e., using bombardment by energetic ions on the substrate during deposition. Because of the essential role of these ions in all the preparation methods "*i*-C" has been proposed as a generic term for this amorphous diamondlike carbon (DLC),[17] a designation similar to *a*-Si for amorphous silicon.

Thermodynamically, diamond is in a metastable state of equilibrium at atmospheric pressure and room temperature. Therefore, synthetic, as well as natural, diamonds typically are formed only under extreme conditions of pressure and temperature. In order to interpret the formation of metastable structures, including microcrystallites of diamond in *i*-C films as observed by some authors,[13,14,17] the occurrence of temperature and pressure spikes at the instant of ion bombardment has been proposed as taking place on the deposition surface[17,18] based on the concepts of Seitz and Koehler.[19] For ions with an energy of 100 eV, the calculated temperature and pressure spikes are at least 3823 K and 1.3×10^{10} Pa (1.2×10^{5} atm), respectively, over a time period of 7×10^{-11} s, which is long compared with the vibration period of 2.6×10^{-14} s obtained from the Debye temperature of diamond. This suggests that a diamond nucleus of about 1 nm may be formed by the thermal agitation and the shock wave accompanying the ion impingement on the surface. Therefore, during *i*-C deposition the carbon atoms might combine at the surface to form all possible combinations of sp, sp^2, and sp^3 bonds. Hexagonal graphite would be formed with planar sp^2 bonds, whereas tetrahedral sp^3 bonding results in the formation of cubic diamond. Furthermore, the preservation of these rather metastable atomic arrangements is understandable because of the extremely high quenching rates associated with the rapid collapse of the spikes. Both atomic agitation and rapid quenching accompanying the condensation of energetic species are important to the understanding of the nonequilibrium process of *i*-C deposition. To render the cooling process rapid enough to prevent the transformation of metastable phases into graphite, a reactive pulsed plasma (RPP) was used in preparation of *i*-C.[20] The essential feature of the method is a homogeneous nucleation on carbon ions in the gas phase which allows carbon nuclei of crystallization to be formed with structures characterized by an increased energy of electron configuration.[21] The nucleation of ions gives rise to thermodynamic conditions corresponding to the pressure–temperature regime in which diamond is stable. Finally, owing to the very high speed of electrodynamic expansion of the plasma generated in a coaxial accelerator, the RPP method permits the crystallization products to remain in their metastable phase state with an increased internal energy.

Another aspect of importance is the simultaneous distillation process due to ion etching.[12] This material removal process is believed to be done mainly by Ar ions.[22] This results in preferential removal of the less tightly bonded carbon and gas atoms, leading to the buildup of those atoms having the strongest bonds. Thus the simultaneous ion beam etching process also has profound effects on the final structure and properties of *i*-C films. As a result of simultaneous energetic impacts of carbon ions and sputtered species, a small fraction of the carbon can form microcrystallites of metastable phases in deposited films which are almost totally amorphous.

On the other hand, the radiation damage caused by impinging energetic species must be expected to impair certain film properties, and an upper limit of the mean particle energy is set by the critical value above which resputtering predominates over condensation. For example, whereas the car-

bon films deposited by ion beam plating at ion energies of 100 to 250 eV exhibited diamondlike properties, an increase in the ion energy to values on the order of 1 keV caused notable changes in the films, which were found to be less hard and of dark brownish color, instead of optically transparent up to 3 μm in thickness as observed when moderate voltages were applied.[23] These variations in the film properties with increasing ion energy were interpreted by the assumption that the defects caused by impinging energetic species can agglomerate to form graphite segregations.[24]

The effects of cobombardment of energetic particles on carbon films can be illustrated by a comparison of film properties prepared by various methods and at different conditions. The amorphous carbon films prepared by vacuum evaporation generally have a room-temperature electrical resistivity of between 10^{-1} and 1 Ω cm (Ref. 25) and absorb heavily in the visible and ultraviolet ranges.[26] It was suggested that there is a high density of gap states in evaporated carbon because a large portion of the carbon atoms are bonded graphitically, whereas in glow discharge carbon a larger pseudogap and lower density of gap states are a result of the mixed bonding in which the presence of the tetrahedral carbon prevents the development of an extended graphitic structure with threefold coordination.[27] Therefore, the electrical resistivity of carbon films deposited by the glow discharge decomposition of acetylene is up to 12 orders of magnitude greater than the evaporated carbon.[27] This is also true for the carbon films produced by condensation of carbon ions with energies in the range of 40 to 100 eV, i.e., low-energy carbon ion beam deposition,[11,12] but to a lesser extent for the carbon films formed by sputter deposition,[28-30] because of the lower energy (about 10 eV) of sputtered carbon ions. For the purpose of a complete comparison of film properties between condensation of carbon ions and sputter deposition, various properties observed by different authors are summarized in Table I. It is clear that the properties of carbon films are closely related to the preparation conditions, e.g., the higher ion energy leads to more diamondlike properties.

The relationship between film properties and deposition conditions becomes more complicated in the most studied method for *i*-C film preparation, viz., decomposition of hydrocarbon gas in a glow discharge, because hydrogen is also provided to the growing layers. This suggests that at low ion energies the formation of some kind of polymer may be expected.[31] With increasing ion energies, the extent of cracking of the hydrocarbon species increases until finally all the hydrogen may be stripped off as a result of energetic impacts, since the C–C bond strength (607 kJ/mol) is greater than that of C–H (337.2 kJ/mol).[32] Therefore, carbon atoms may

TABLE I. Summary of film properties prepared by ion beam and sputter deposition.

Deposition conditions			Properties of hard *a*-C films					
Deposition method	Source of carbon	Ion energy (eV)	Density (g/cm^3)	Electrical resistivity (Ω cm)	Optical properties		Hardness (kg/mm^2) (HV or HK)	Chemical inertness
Condensation of carbon ions (ion beam deposition)	Carbon in rf plasma[a]	40–100		$\sim 10^{10}$		Refractive index, $n = 2.0$	> glass	Resist HF for 40 h; 10–20 yr archiv lifetime
	Carbon in arc[b]	50–100		$> 10^{12}$		$n \sim 2$		
	Carbon in dc plasma[c]	50–100			Dielectric constant ~ 6 (diamond = 5.7)	$n = 2.3$ at $\lambda = 5\ \mu m$	1850 HK (diamond = 7000 HK)	
Sputter deposition	Carbon target in rf plasma[d]	rf power = 2.25 and 75 W		10^{-3}–10^{3}	Optical gap, $E_0 \sim 0.8$ eV			
	Carbon sputtered by Ar^+ beam[e]	1–20	2.1–2.2	$> 10^{11}$	Reflectance 0.2 Absorptance 0.7 Absorption coefficient, $\alpha = 6.7 \times 10^4\ cm^{-1}$ transmittance 0.1			
	dc magnetron sputtering of a graphite target[f]	Sputtering power density (W cm^{-2})		(at 300 K)	n (at $\lambda = 1\ \mu m$)	E_0 (eV)	HV	
		0.25	2.1–2.2	2.5×10^{3}	2.4	0.74	2410	
		2.5	1.9	1.0	2.73	0.50	2015	
		25	1.6	0.2	2.95	0.40	710	

[a] Reference 11. [b] Reference 12. [c] Reference 31. [d] Reference 28. [e] Reference 29. [f] Reference 30.

accumulate on the substrate while hydrogen atoms are sputtered off.[33] The infrared (IR) absorption results show that the hydrogen concentration in the film is only a few percent when the substrate potential V_s is kept at 200 V. Above this value it becomes almost negligible.[33] Evidence for this is the absence of, or very weak, absorption bands for C–H bonds in the IR transmission spectra.[34] However, some of the released hydrogen could become incorporated in the growing carbon film. As much as 25 at. % H was found by the Rutherford backscattering spectroscopy (RBS) analysis in some *i*-C films.[35] This group of *i*-C films is loosely called hydrogenated amorphous carbon films (*a*-C:H), covering from the polymeric carbon (a-CH_x) films produced at minimal bombardment[36] to diamondlike hard carbon films produced over an ion energy range of several hundred electron volts.[37]

The application of glow-discharge decomposition to *i*-C film production was introduced in the midseventies and has been developed rapidly since. The use of these films in a number of technological fields has been explored, such as for wear- and corrosion-resistant coatings in sliding devices, antireflection coatings, protective coatings or hermetic seals for optics, dielectric *p*–*n* junctions, barrier coatings, passivation layers, and heat sinks in electrical devices.[38] It is impractical to cover here all the works in this area because of the emphasis of the present paper on the magnetic recording applications. However, it is important to review briefly some of the observations made with *i*-C films deposited by ionized hydrocarbon species.

The Vickers hardness of *i*-C films was found to increase with substrate potential V_s.[33] At an optimum value of V_s a maximum hardness can be achieved.[37] This indicates the contribution to the diamondlike properties of impingement on a growing layer by the energetic ions. However, resistivity ρ appears to decrease with increasing V_s.[33] This may be interpreted in terms of the change of hydrogen concentration. It was found by nuclear reaction analysis that the hydrogen content in *i*-C films decreases with increasing V_s up to 700 V.[39] It is also known that resistivity is increased profoundly by hydrogen,[40] because the ratio of fourfold to threefold coordinated carbon atoms increases when more hydrogen is present in the *i*-C film. (The fully threefold coordinated form of carbon, graphite, has a zero energy gap, whereas diamond with the fully fourfold coordination has a 5.4-eV energy gap.[41])

This is merely one of the many complications caused by the presence of hydrogen in *i*-C films. Thus, the variety of solid-state structures and properties of hydrogenated *i*-C films, although consisting predominantly of carbon, appears to be more diverse than the pure carbon material which already covers a wide range of properties by the unique capability of its atoms to form chains, rings, or combinations of different patterns which constitute the framework of the variety of structure.

It is interesting to note that *i*-C films exhibit extremely low values for the friction coefficient: μ decreases from 0.9 to 0.04 after 10^4 cycles, between an *i*-C disk and steel ball,[37] and $\mu = 0.005$–0.02 against a steel ball under vacuum.[42] This resembles diamond except that the μ of diamond against polished steel does not show a marked dependence on humidity as *i*-C films do and it remains below 0.07 even for a relative humidity of nearly 100%.[43] For comparison, the static μ for iron on itself in vacuum is 1.5, in air is 1.0, and for steel $\mu = 0.8$.[43]

Although typical hydrogenated *i*-C films are characterized by high resistivity ($10^{13}\ \Omega$ cm,[44] 10^{9}–$10^{12}\ \Omega$ cm,[33] and 10^{7}–$10^{10}\ \Omega$ cm[37]) and extreme hardness, the reported values of microhardness of sufficiently thick films vary significantly among different authors. The Knoop hardness of *a*-C:H films deposited from benzene vapor in a rf plasma ranges between 1250 and 1650 kg/mm^2 for a 100-g load, after the influence of the substrate is eliminated.[44] The Vickers hardness at a load of 40 g measured on *i*-C films prepared by ion beam plating from benzene are in the range of 3363 to 5706 kg/mm^2, corresponding to a maximum hardness of 9.4 Mohs.[37]

Another characteristic of *i*-C films distinguishing them from ordinary amorphous carbon is their chemical inertness. The *i*-C films are impervious to reagents which dissolve graphitic and polymeric carbon structures.[45] Some CH_4-derived films on silicon were kept for four years and showed no visible signs of deterioration.[45]

The optical properties also make *i*-C films closer to those of diamond (a large-band-gap semiconductor) than those of graphite (a semimetal). By increasing the hydrogen concentration, the band gap is increased to a maximum value, thus causing the films to become increasingly transparent. The optical properties of *i*-C films will be elaborated on later in connection with structure characterization.

Some characteristic properties of hydrogenated carbon films prepared in different systems are summarized in Table II. The hydrogen content of the films, which varies in a wide range, is also included. When a glow discharge is excited in a hydrocarbon gas at low pressure, both ionized and neutral components of the fragmented hydrocarbon bombard the substrate. At low power densities the degree of hydrocarbon dissociation both in the gas phase and from ion impact at the substrate is insufficient to break all C–H bonds. A polymer film is accordingly formed. As the power input increases, the rupture of C–H bonds and sputtering of hydrogen become increasingly enhanced. The hydrogen remaining in the carbon films may simply bury in the free state. In other words, the hydrogen may be present in a bound and an unbound form. The amount of chemically bonded hydrogen as determined by IR spectroscopy is found to be less than the total hydrogen content measured by nuclear reaction analysis and combustion analysis.[53] The amount of unbound or chemisorbed hydrogen on *a*-C:H films has been determined by differential scanning calorimetry (DSC).[54] In another study of *a*-C:H films, the absolute hydrogen concentration was found to be as high as 47 at. % by proton recoil spectroscopy. However, because of the uncertainties in IR absorption data the fraction of bound hydrogen was not determined.[37]

In regard to structure, the hydrogen incorporated in the *a*-C:H films may play a crucial role in the bonding configuration of the carbon atoms by helping to stabilize tetrahedral coordination (sp^3 bonding) of the carbon atoms, which is

TABLE II. Summary of properties of hydrogenated carbon films

Deposition system	Film density (g/cm^3)	Optical properties	Electrical resistivity (Ω cm)	Hydrogen content	Vickers or Knoop hardness, kg/mm^2 (HV or HK)
C_2H_2 in a dc glow discharge[a]	1.35	Optical gap, $E_0 = 2.2$ eV	$> 10^8$		
Ion beam of CH_4 + Ar (molar ratio = 0.28)[b]	1.8	$E_0 = 0.38$ (dual beam 0.34)	8.7×10^4 (3.3×10^4)	H/C = 1.0	
rf plasma using CH_4, C_2H_6, propane, propylene[c]		$E_0 = 2.7$	$> 10^{13}$		5–6 Mohs
C_2H_2 in a dc glow discharge[d]	1.2–1.3	$E_0 = 1.8$	$> 10^9$		
CH_4 in a rf glow discharge (50–500 W)[e]		$E_0 = 2.7$	$< 10^{13}$		
C_2H_2 (4–30 vol %) + Ar at 10–100 mTorr of glow discharge[f]		$E_0 = 0.75$	10^2–10^3	Very low hydrocarbon content	2000–2800 HV
CH_4 or C_4H_{10} in a rf discharge[g]	2.0–2.67		10^{12}	H/C = 0.29–0.42	
dc magnetron sputtering in an Ar–C_2H_2 plasma[h]	1.13–1.27	$E_0 = 1.15$–2.0	$> 10^7$	H/C = 0.25–0.84	
C_6H_6 in a rf glow discharge[i]	1.5–1.8	$E_0 = 0.8$–1.8	10^{12}	H/C ~ 0.5	1250–1650 HK
C_4H_8 in a rf glow discharge[j]	1.55	$E_0 = 1.2$	$> 10^{12}$	H/C ~ 0.65	1250–1650 HK
C_2H_2 in a dc glow discharge[k]			$> 2\times10^5$		2000 HV
Acetylene in a rf glow discharge[l]	1.7	$E_0 = 1.5$–2.6	10^{13}		
Various hydrocarbons in a rf glow discharge[m]	1.5–2.0		10^9		3000 HV
dc ion decomposition of benzene, toluene at ion energies[n] (A) 250 eV (B) 800 eV	> 2.0 at 100–250 eV ion energies	Refractive indices at λ = 546.1 nm (A) $n_1 = 2.8$ (B) $n_2 = 2.3$	$> 10^{10}$		(A) ~5000 HV (B) ~3000 HV
C_2H_2 in a dc glow discharge[o]		$E_0 = 0.9$–2.1	10^4–10^{14}		
Butane in a rf plasma[p]		$n_1 = 2.3$ (λ = 5 μm)			1250 HK
CH_4 in a dc glow discharge[q]			10^9–10^{14}		1700–2700 HV
rf discharge of CH_4 with selfbias voltage[r] (A) < 100 V (B) 100–800 V		Dielectric constant ε (A) 2–4, (B) 6–10	(A) 10^9–10^{13} (B) 10^6–10^9		
Single or dual ion beam of CH_4 + Ar (ratio = 0.25)[s]		$E_0 = 0.9$–1.1 eV ε = 3.0	8.1×10^4	7 at. % H	
Electron-assisted chemical vapor deposition with a mixture of $CH_4 + H_2$ (2 vol % CH_4, 823 K)[t]	2.8	Thermal conductivity ≈ 1100 W (m K)$^{-1}$	$> 10^{13}$	A light peak of C–H bond in stretch mode in IR spectra	~ 10 000 HV

[a] Reference 46. [b] Reference 45. [c] Reference 47. [d] Reference 36. [e] Reference 48. [f] Reference 34. [g] Reference 35. [h] Reference 49. [i] Reference 44. [j] Reference 50. [k] Reference 51. [l] Reference 37. [m] Reference 52. [n] Reference 33. [o] Reference 41. [p] Reference 31. [q] Reference 33. [r] Reference 53. [s] Reference 54. [t] Reference 14.

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MICROSTRUCTURES OF HYDROGENATED AMORPHOUS CARBON FILMS PREPARED BY RF PLASMA CVD

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Hydrogenated amorphous carbon (a-C:H) films are prepared by rf plasma CVD and changes in their microstructures due to the substrate bias (Vs) and temperature (Ts) have been investigated by TEM, FT-IR, Raman spectroscopy and ellipsometry. When Vs increases to positive, the substrate current (Is) increases steeply at around Vs=250 V, and the structure of the film is remarkably affected by Is rather than Vs. The films deposited at lower Is and Ts have homogeneous and amorphous structures containing sp^3CH_n configurations. Upon increasing Is and Ts, the hydrogen content (hydrogenation) decreases and the structure comes to be fine grain-like, which caused by increase of threefold-coordinated (sp^2) configurations as in graphite.

1. INTRODUCTION

Considerable attention has been paid to hydrogenated amorphous carbon (a-C:H) films. The films are fabricated by various plasma CVD techniques, and their structures and properties are remarkably different with the deposition conditions.

When a negtive bias voltage (Vs) is applied the substrate, the average energy of ions impinging on the substrate increases, and the properties of the films are remarkably different.[1,2] On the other hand, when Vs is positive, electrons impinging on the substrate increase, and the impact of the ionic species are suppressed or eliminated. The structure of a-C:H also apparently with positive Vs. Our previous results have shown that the microstructure of a-Si:H films prepared by ion plating technique remarkably change from amorphous to microcrystalline when Vs is changed from negative to positive.[3]

While, in contrast to tetrahedrally (sp^3) bonded silicon in the a-Si:H, the carbon atoms in the a-C:H film are bonded with three different types, which results in sp^1, sp^2, sp^3 and their hybrid configurations. Furthermore, reactions between atomic hydrogen produced by the discharge and the deposits on the substrate affect the structure of the films. These reactions eliminate the weak bonds in the films, and are accelerated by the substrate temperature (Ts).

Then it can be considered that the structure of the a-C:H changes by both Vs and Ts. In this paper, to make these view points clear, a-C:H films are prepared by rf plasma CVD technique and changes in their microstructures due to Vs and Ts have been investigated.

2. EXPERIMENTAL

The scheme of the rf plasma CVD system used in the present experiment is shown in Fig. 1. Plasma of CH_4 diluted with H_2 is produced around rf coil which is inductively coupled to the rf power source at 13.56 MHz. The filament of tungsten is placed between the substrate and the rf coil in order to heat the substrate. The temperature of the substrate (Ts) was measured by the thermocouple in contact with the surface on the substrate. The substrate of about 64cm²

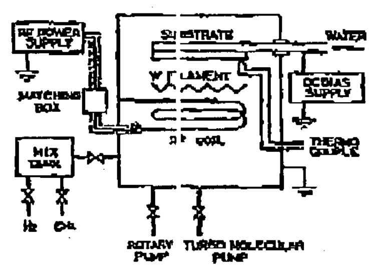

FIGURE 1
Schematic diagram of the rf plasma CVD apparatus used in the present work.

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in area was biased by the dc bias supply, and the current of it (I_s) was controlled by changing the dc bias voltage.

After the chamber was pre-evacuated to less than 10^{-3} Pa by a turbo molecular pump, the mixture of CH_4-H_2 gases, where the ratio of $CH_4/(H_2+CH_4)$ are 10 %, was introduced to the system. The gas flow rate and total pressure during the deposition were 10 sccm and 2.2 Pa, respectively. Silicon wafers were used as the substrate for the measurements of FT-IR, ellipsometry and Raman spectroscopy. Samples observed by TEM were deposited on thin aluminum substrates, and then they were mounted on the copper grids after dissolving the substrates in sodium hydroxide solution.

The Raman spectra were measured with 514.5 nm line of Ar ion laser, and the beam was condensed to 1 μm in diameter to avoid contaminated portions on the samples. Optical constants (n,k) of the films were calculated from the ellipsometric measurement using 632.8 nm line of He-Ne laser.

3. RESULTS AND DISCUSSION

When Vs increased to positive direction, Is increased steeply at around Vs=250 V ; Is=50, 150 and 280 mA at Vs=230, 280 and 300 V, respectively. The structure of the films was remarkably affected by Is rather than Vs, as shown hereafter.

Figure 2 shows the infrared absorption spectra of C-H stretching vibration when Vs(Is) and Ts are changed. The absorption bands due to stretching vibrations of sp^3 and sp^2 C-H bonds reported by Dischler et al.[4] are also shown in

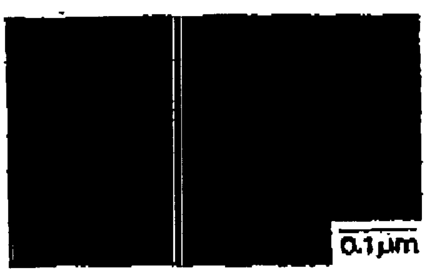

FIGURE 3
Transmission electron micrograph of the film deposited under Vs=300 V, Is=280 mA and Ts=100°C.

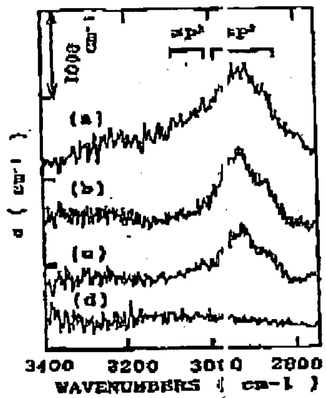

FIGURE 2
FT-IR spectra of the films when Vs(Is) and Ts are changed as follows.
(a) Vs=-100 V, Is=-15 mA, Ts=20°C
(b) Vs=+230 V, Is=+50 mA, Ts=20°C
(c) Vs=+260 V, Is=+150 mA, Ts=20°C
(d) Vs=+260 V, Is=+150 mA, Ts=100°C

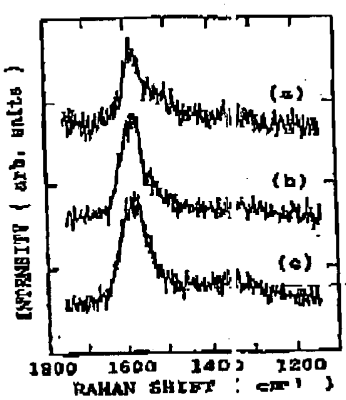

FIGURE 4
Raman spectra of the films when positive Vs(Is) and Ts are changed as follows.
(a) Vs=260 V, Is=150 mA, Ts=20°C,
(b) Vs=260 V, Is=150 mA, Ts=100°C
(c) Vs=300 V, Is=280 mA, Ts=100°C.

formation of H_2

Fig. 2. The sp^3 C-H absorptions are dominant, and decrease when Vs(Is) is increased to positive direction as shown by (a), (b) and (c). The absorption is more drastically decrease due to the increase of Ts as shown by (c) and (d). These results show that hydrogen atoms consisting the C-H bonds in the film are extracted by attacking atomic hydrogens during the deposition as well known, and this reaction is enhanced by the increase of Vs(Is) and Ts.

Corresponding to the decrease of the IR absorption, the microstructure observed by TEM changed from homogeneous to grain-like. Figure 3 shows a micrograph observed by TEM when Vs(Is) and Ts are 300 V (280 mA) and 100°C, respectively. Micro-grains observed in this micrograph appear when the IR absorption shown in Fig. 2 diminishes at higher Vs(Is) and Ts.

Figure 4 shows Raman spectra of the films when Vs(Is) and Ts are changed. With increasing Ts, as shown by (a) and (b), and Vs(Is), as shown by (b) and (c), a peak at around 1580 cm^{-1} comes to be clear, and a broad peak at around 1350 cm^{-1} appears. It has been reported that these two peaks are considered to originate from carbon clusters with an sp^2 configuration,[5-8] and relative intensity of the 1350 cm^{-1} peak against the 1580 cm^{-1} peak increases with increasing the crystallite size.[9,10] Then the present results show that the films contain sp^2 bonded clusters, and their sizes increase with increasing Vs(Is) and Ts.

Table I shows refractive index (n) and absorption index (k) obtained by the measurement of the ellipsometry. The n and k increase with increasing Is and Ts. The increases of these optical constants mean the increase of graphitic sp^2 component.[11] Then this result is consistent with above results.

TABLE I.
Refractive index n and absorption index k determined by ellipsometry.

Bias	Substrate Temperature			
	20°C		100°C	
	n	k	n	k
-100V/15mA	1.9-2.0	0.01-0.00	1.9-2.0	0.08-0.00
+260V/150mA	1.9-2.0	0.07-0.03	2.1-2.3	0.62-0.58
+300V/280mA	2.2-2.3	0.60-0.62	2.2-2.3	0.60-0.80

4. CONCLUSIONS

Hydrogenated amorphous carbon films were prepared by rf plasma CVD technique and the changes of their microstructures due to Vs(Is) and Ts were investigated.

When Vs(Is) and Ts are relatively low, the structure of the film is homogeneous and contains sp^3C-H configurations. When Vs(Is) and Ts increase, the C-H bonds decrease due to the reactions with the atomic hydrogens during the deposition, and the film comes to contain fine grain-like structures consisted with sp^2 configurations. These changes of microstructures due to the increase of Vs(Is) and Ts result in the increases of refractive index (n) and absorption index (k).

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